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HYDROGEN PERMEABILITY OF MICROSPHERES BASED ON ASH AND SLAG

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The compositions of aluminosilicate microspheres made of TPP ash and slag are investigated. A correlation-regression analysis of the criteria characterizing the glass structure is implemented. The role of the components and the effect of the structure cohesion, internal porosity, molar volumes of oxides, and aluminosilicate and silicate moduli on hydrogen permeability of microspheres is established. A composition promising for designing microspheres for use as gas containers is identified.

Microspheres are used in physical experiments as hydrogen containers [1], but there is no established method for designing such glass. At the same time, ash and slag generated by thermal power plants (TPP) are a substantial source of material for spheres with a low content of alkali R_2O and alkali-earth RO oxides [2]. Therefore, it appears convenient to study the component composition of microspheres based on ash and slag and the criteria *Kr* responsible for their structure: the hydrogen permeability coefficient *K*, the molar volume V_i, the silicate n_{Si} and aluminosilicate n_{AlSi} modulus, the structure cohesion factor *Y*, and the internal porosity P_{int} [3 – 8]:

$$K = 8.1 \times 10^{-14} \exp\left[-\frac{1}{T}(17{,}330 - 127.8G)\right];$$

$$V_i = m_i \overline{V}_i;$$

$$n_{Si} = \frac{C_{SiO_2}}{C_{Na_2O}};$$

$$n_{AlSi} = \frac{C_{SiO_2} + C_{SiO_2}}{C_{Na_2O} + C_{K_2O}};$$

$$Y = \frac{\sum_j x_j C_j z - \sum_k x_k C_k}{\sum_j x_j C_j};$$

$$P_{int} = 100\left(1 - \frac{\sum V_i}{V_{Si}}\right),$$

where *T* is the temperature, K; *G* is the content of glass-forming agents in the case considered ($C_{SiO_2} + C_{P_2O_5}$), % (here and elsewhere molar content); *m* is the molar part of oxide; *i* is the ordinal number of the component; $\overline{V}$ is the partial molar volume of oxide, cm^3/mole [4]; *C* is the component content, %; x_j and x_k are the number of cations; *j* are oxides containing cations with number of bonds equal to unity (R_2O); *z* is the valence; *k* are oxides containing cations *x* with number of bonds greater than one; ΣV_i is the sum of oxides without SiO_2.

When data on $\overline{V}$ were missing, the volumes V_i were calculated based on the formula in [9] taking into account the molar part m_i, molar weight M_i, and density ρ_i of the oxide:

$$V_i = \frac{m_i M_i}{\rho_i}.$$

The results of calculation of *Kr* are given in Table 1. The aluminosilicate microspheres [2] contain 11 components: modifying oxides (*mod*) R_2O ($C_{Na_2O} + C_{K_2O}$ = 1.05 – 6.56%) and RO ($C_{CaO} + C_{MgO}$ = 4.20 – 7.09%). The silica content was 64.64 – 72.40% and that of alumina 13.16 – 21.72%; the amount of Al_2O_3 mostly deceased with increasing SiO_2 content and was equal to no more than one-third of C_{SiO_2}. P_2O_5 was present as an impurity (0.03 – 0.29%). All compositions contained Fe_2O_3 (0.27 – 2.86%) and TiO_2 (0.60 – 1.97%), whereas about half of the compositions at the same time contained FeO and MnO (1.70 – 4.97 and 0.04 – 0.41%, respectively). This is probably related to the redox processes occurring in the combustion of coal and

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formation of microspheres. The oxide content in the averaged composition of microspheres based on ash and slag is as follows (%): 66.86 SiO_2, 0.89 TiO_2, 19.90 Al_2O_3, 1.73 Fe_2O_3, 2.92 FeO, 1.09 CaO, 3.12 MgO, 0.10 MnO, 3.05 K_2O, 1.06 Na_2O, and 0.09 P_2O_5 (Fig. 1). The averaged composition is based on eight components: the oxides of Si, Ti, Al, Fe(II, III), Ca, Mg, K, and Na (SiO_2, Al_2O_3, CaO, MgO, K_2O, and Na_2O are traditionally used in making chemically resistant glassware for chemicals in different aggregate states).

In order to identify the *Kr* affecting *K*, *Y*, and P_{int} of ash- and slag-based microspheres, a correlation regression analysis was performed in accordance with the method described in [10]. The regressions were approximated using functions of the type of $Y(X) = A + BX$. Table 2 gives the results corresponding to the correlation coefficient $|R| \geq 0.5$. It is established that SiO_2, K_2O, and Al_2O_3 can influence most perceptibly the permeability of microspheres. The signs of the coefficients *R* coinciding with the signs of the second summands of the regression equation (BX) indicate the direction of this effect: the positive sign indicates an increase and the negative sign indicates a decrease in permeability: SiO_2 will increase and Al_2O_3 and K_2O will decrease the permeability of glasses, same as all modifiers (Na_2O, K_2O, MgO, and CaO).

The high value of the cohesion factor $Y_{av} = 3.50$ representing the average number of bridge oxygen ions per one structural polyhedron shows that the structural lattice of microsphere glasses can be half-formed by three-dimensional patterns consisting of ordered tetrahedra [SiO_4]. This is undesirable for storing gaseous materials in glass articles, since quartz glass and glasses rich in SiO_2 (ash and slag microspheres) are the most gas-permeable [11, 12]. The decrease in permeability due to the presence of R_2O is related to its modifying effect. The role of Al_2O_3 is more complicated, which is shown by the parabolic shape of curve *2* (Fig. 2*a*). Its branches point downwards. This shows that as the content of Al_2O_3 changes in accord with the branch on the left from the extremum (compositions 9 – 1), permeability increases, whereas the right branch (compositions 9 – 17) indicates decreasing permeability. A part of Al_2O_3 presumably exists in the form of tetrahedra [AlO_4], for which R_2O and RO are oxygen donors [12].

The formation of structural patterns due to Si – O – Al bonds facilitates an increase in glass permeability. This is corroborated by a high value of the coefficient *R* (0.79) for $\log K = f(n_{AlSi})$, i.e., the probability of Al_2O_3 participating along with SiO_2 in structure formation is very high. It can be assumed that when non-bridge oxygen ions are redistributed

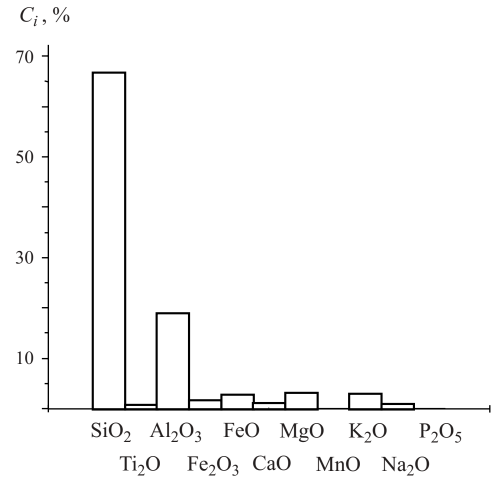

Fig. 1. Histogram of component distribution based on their molar contents in the averaged composition.

TABLE 1

Composition	TPP	n_{Si}	n_{AlSi}	Y	P_{int}	log *K*	V_i, cm³/mole										
							SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	MnO	K_2O	Na_2O	P_2O_5
1	Vladimirskaya TPP-1	59.83	28.90	3.51	56.84	– 25.04	28.34	0.18	7.92	0.52	0.42 – 0.57	0.40	0.83	0.01	1.47	0.36	0.12
2	Zaporozhaskaya	67.20	29.66	3.53	46.45	– 25.27	26.46	0.25	10.83	1.14	–	0.13	0.51	–	0.95	0.30	0.06
3	Moskovskaya TPP-22	104.20	28.96	3.53	49.64	– 25.34	27.42	0.59	10.42	0.14	–	0.23	0.33	0.08	1.19	0.20	0.06
4	Krivorozhskaya	110.50	39.71	3.53	43.64	– 25.37	26.12	0.29	11.07	1.24	0.44	0.16	0.56	–	0.78	0.56	0.06
5	Starobeshevskaya	44.06	18.91	3.46	40.26	– 25.65	25.36	0.25	11.27	1.00	–	0.13	0.44	–	1.50	0.44	0.12
6	Kurakhovskaya	69.46	25.93	3.47	41.99	– 25.87	25.41	0.25	10.99	0.72	–	0.11	0.72	0.01	1.16	0.28	0.06
7	Zmievskaya	62.99	20.73	3.49	35.54	– 25.84	24.65	0.20	12.16	0.93	–	0.17	0.36	–	1.53	0.30	0.24
8	Slavyanskaya	47.32	17.31	3.47	36.62	– 25.95	24.66	0.27	11.51	0.96	–	0.20	0.49	0.005	1.74	0.40	0.06
9	Luganskaya	152.80	22.64	3.52	33.84	– 26.02	24.20	0.29	12.00	1.17	–	0.26	0.41	–	1.64	0.12	0.12
10	Zuevskaya	94.24	23.58	3.45	38.82	– 26.10	24.74	0.23	11.23	0.62	0.72	0.14	0.53	0.01	1.43	0.30	0.03
11	Shahktinskaya	54.66	16.75	3.44	35.46	– 26.13	24.31	0.18	11.07	1.17	–	0.30	0.69	0.01	1.88	0.34	0.06
12	Pridneprovskaya	42.54	17.24	3.44	35.64	– 26.20	24.41	0.23	11.59	0.62	0.30	0.30	0.51	–	1.67	0.44	0.04
13	Uglegorskaya	72.59	23.03	3.43	38.48	– 26.26	24.61	0.23	11.19	0.11	0.89	0.03	0.73	0.01	1.36	0.26	0.03
14	Nesvetaevskaya	56.81	13.92	3.44	32.06	– 26.27	23.77	0.31	11.03	1.24	–	0.13	0.65	–	2.35	0.32	0.12
15	Mironovskaya	54.86	19.30	3.43	35.23	– 26.30	24.21	0.23	11.55	0.65	0.53	0.03	0.73	0.01	1.57	0.34	0.04
16	Tripolskaya	48.38	14.85	3.44	35.03	– 26.29	23.95	0.27	10.58	1.38	–	0.92	0.44	–	1.47	0.38	0.12
17	Novocherskasskaya	56.70	12.93	3.40	30.68	– 26.53	23.60	0.21	11.43	0.59	0.40	0.17	0.61	0.01	2.59	0.32	0.03

TABLE 2

$Y(X)$	X	$Y(X) = A + BX$	R
$\log K$	V_{SiO_2}	$-33.62 + 0.31V_{SiO_2}$	0.94
	V_{K_2O}	$-24.83 - 0.71V_{K_2O}$	–0.76
	$V_{Al_2O_3}$	$-22.91 - 0.27V_{Al_2O_3}$	–0.58
	V_{mod}	$-24.37 - 0.58V_{mod}$	–0.71
	P_{int}	$-28.17 + 0.06P_{int}$	0.91
	Y	$-57.13 + 9.00Y$	0.87
	n_{AlSi}	$-26.98 + 0.05n_{AlSi}$	0.79
Y	V_{SiO_2}	$2.89 + 0.02V_{SiO_2}$	0.73
	V_{K_2O}	$3.57 - 0.06V_{K_2O}$	–0.71
	V_{mod}	$3.63 - 0.06V_{mod}$	–0.77
	n_{AlSi}	$3.365 + 0.005n_{AlSi}$	0.80
	n_{Si}	$3.411 + 0.001n_{Si}$	0.58
P_{int}	V_{SiO_2}	$-88.31 + 5.09V_{SiO_2}$	0.99
	V_{K_2O}	$56.29 - 11.26V_{K_2O}$	–0.77
	$V_{Al_2O_3}$	$103.26 - 5.80V_{Al_2O_3}$	–0.78
	V_{mod}	$60.97 - 8.27V_{mod}$	–0.64
	n_{AlSi}	$23.31 + 0.72n_{AlSi}$	0.74
n_{AlSi}	C_{SiO_2}	$-144.73 + 2.45C_{SiO_2}$	0.80
	$C_{Al_2O_3}$	$49.49 - 1.42C_{Al_2O_3}$	–0.38
	C_{K_2O}	$36.76 - 4.76C_{K_2O}$	–0.80
	C_{Na_2O}	$35.64 - 12.61C_{Na_2O}$	–0.58
$V_{Al_2O_3}$	V_{SiO_2}	$24.04 - 0.52V_{SiO_2}$	–0.74

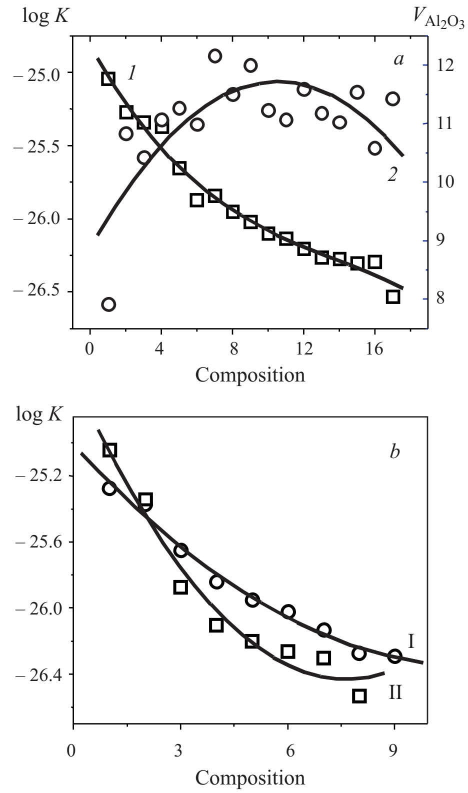

Fig. 2. Variations in structure-determining criteria for microspheres based on TPP slag and ash: *a*) log *K* (*1*) depending on molar volume $V_{Al_2O_3}$ (*2*); *b*) variations in log *K* in subgroups I and II.

in the voids of the silicon-oxygen lattice and octahedral polyhedra are formed, the porosity will decrease [12]. Since $C_{Al_2O_3}$ is substantial and C_{R_2O} and C_{RO} are rather low (Fig. 1), it is highly probable that aluminum exists in the six-coordination state with respect to oxygen and acts as a modifier.

The criterion Y significantly depends on which part of the structure is occupied by the main lattice-forming component (in the case of P_{int} this is SiO_2 summed with Al_2O_3), as well as the modifiers, especially K_2O (Table 2). The criteria Y and P_{int} depend more on n_{AlSi} than on n_{Si}; the value R for $Y = f(n_{Si})$ indirectly confirms that the lattice is mainly formed by SiO_2, but with participation of Al_2O_3 ($R = 0.74$ for $P_{int} = f(n_{AlSi})$). A decrease in n_{AlSi} will presumably correspond to decreasing P_{int} due to a decreased content of the lattice-forming agents or an increased amount of the modifiers. This will decrease the dimensionality of the lattice, which is favorable for making glasses with low gas permeability.

The main contribution to the aluminosilicate modulus is made by the content of SiO_2 ($R = 0.8$ for $n_{AlSi} = f(C_{SiO_2})$); Al_2O_3 acts as an additional lattice-former, since $R = 0.38$ for $n_{AlSi} = f(C_{Al_2O_3})$. Note that when studying glasses in which the Al_2O_3 content exceeds 1/5 of the composition, it is convenient to use the aluminosilicate modulus, which adequately reflects the structural specifics.

A high correlation of the dependence of permeability on P_{int} ($R = 0.91$) and Y ($R = 0.87$) appears logical; as the cohesion of the structural lattice increases, which makes it more ordered and more similar to the quartz structure, the porosity and permeability of the structural glass lattice grow, and vice versa.

The slag-and-ash microspheres were divided into subgroups: FeO and MnO were absent in the first subgroup and all components were present in the second subgroup. The impermeability variation curves for these subgroups are indicated in Fig. 2*b*. The equality of log *K* at the point of intersection of curves I and II is reached by raising the Al_2O_3 content by 2.67%, the K_2O content by 0.87%, Fe_2O_3 content by 0.48%, and the content of CaO by 0.37%., whereas the content of MgO decreases by 1.97% and that of SiO_2 remains virtually constant.

The averaged compositions and the deviations in the content of oxides Δ in subgroups I and II before and after the curve intersection are calculated from the formulas

$$\Delta_{I(II)} = C_{I(II)\text{-}1} - C_{I(II)\text{-}2};$$

$$\Delta = 100[\Delta_{I(II)}/C_{i,\max}],$$

whereas $C_{i,\max}$ is the highest content of the oxide in the compared compositions.

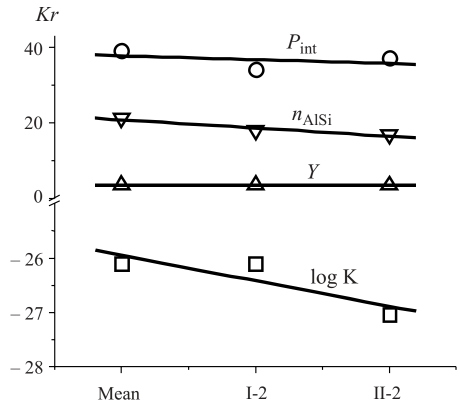

Fig. 3. Variations in factors characterizing the structure of microspheres based on TPP ash and slag in averaged compositions: Mean) composition averaged for all microspheres; I-2) averaged composition for microspheres 7 – 9, 11, 14, and 16; II-2) averaged composition for microspheres 6, 10, 12, 13, 15, and 17.

The decrease in permeability in compositions 7 – 16 in subgroup I (Table 1) is mainly caused by SiO_2 content decreasing by 5% and that of K_2O decreasing by 40%. The same changes in subgroup II are attributed to SiO_2 content decreasing by 10%, CaO by 49%, MnO content by 74%, and K_2O by 39%, whereas the amount of Al_2O_3 increases by 34%, Fe_2O_3 by 54%, and MgO by 27%. Thus, the permeability of slag-and-ash microspheres may decrease even with a small decrease in the content of SiO_2 and a substantial variation in the content of CaO and K_2O; however, the shortage of modifiers can be compensated by Al_2O_3 and Fe_2O_3. Similarly to aluminum, Fe(III) typically exists in the six-coordination state, which leads to the formation of octahedra in the lattice voids [12], i.e., the lattice is modified.

A comparison of the averaged compositions taking into account the reference eight-component compositions and eliminating impurity P_2O_5 as well as FeO and MnO that are not present in all compositions, demonstrated that the increase in the amount of SiO_2 with a simultaneous decrease in the content of Al_2O_3, TiO_2, Fe_2O_3, MgO, and Na_2O can be compensated by increasing the quantity of K_2O and CaO. Due to the effect of isomorphism as the result of the similarity of their ionic radii, the loss of sodium is compensated by calcium $r_{Ca^{2+}} = 0.98$ Å, $r_{Na^+} = 0.95$ Å, and one ion K^+ ($r_{K^+} = 1.33$ Å) is capable of replacing two ions of Mg^{2+} ($r_{Mg^{2+}} = 0.65$ Å) [12, 13].

Figure 3 shows fluctuations in the considered criteria in the averaged compositions. Despite the similarity of numerical values, the composition in subgroup II-2 is more promising for the production of microspheres considering their gas permeability.

As a consequence of the analysis of compositions and structure-determining criteria for microspheres based on ash and slag, it is established that the following composition is promising for designing gas microcontainers (%): 61.99 SiO_2, 0.88 TiO_2, 22.34 Al_2O_3, 1.40 Fe_2O_3, 3.46 FeO, 0.73 CaO, 4.06 MgO, 0.06 MnO, 3.81 K_2O, 1.22 Na_2O, and 0.05 P_2O_5, and the order of mutual replacement of the components is determined.

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